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Purification and Quality Enhancement of Fuel Ethanol to Produce Industrial Alcohols with Ozonation and Activated Carbon

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Abstract. The total ethanol production capacity in the US just passed 6 billion gals/year. The production process of ethanol from corn includes corn milling, cooking, enzymatic starch conversion, fermentation and distillation. Food-grade alcohol production requires more care and undergoes costly additional purification to remove volatile organic impurities. These impurities could be of health concern and/or impart unpleasant tastes and odors to beverage alcohol. Multiple distillation

steps are usually employed. The additional purification of ethanol to obtain food-grade alcohol adds at least $0.30 per gallon in processing costs. In this research, we tested a novel approach to purify fuel grade ethanol to pharmaceutical and beverage grade. The cost of the proposed treatment process is expected to be less than $0.01 per gallon. We have shown that ozone can oxidize a number of undesirable compounds in ethanol. Furthermore, it was demonstrated that adsorption on granular activated carbon can remove many of the ozonolysis byproducts. All chemical and sensory analyses were completed using solid phase microextraction (SPME) to extract volatile organic compounds from ethanol samples and a multidimensional GC-MS-Olfactometry system to identify impurities and the impact of odorous compounds. To date, we confirmed a significant reduction of some impurities with ozone alone. Ozone and granular activated carbon are very effective in purifying fuel ethanol. Also, we designed a purer ozone generating setup. This setup can provide further purification efficiency on this research. This technology will help the corn milling and ethanol industry and provide an opportunity for improving the long-term sustainability of corn growing and processing.

Keywords. Ethanol, purification, ozone, chemical analyses, GC-MS-O

1. Introduction

Ethanol has been utilized since ancient times in fermented drinks for recreational purposes. Also, ethanol is used for various purposes such as disinfection or extraction. Ethanol has recently become even more important as a liquid fuel supplement. Increases in the price of crude oil and the interest in environmental issues have resulted in a rapid increase in the production of fuel ethanol. In 2006, nearly 5 billion gallons of ethanol were produced, and over 100 ethanol plants are now under operation in 20 states (USDA, 2006)., In the United States, ethanol is produced mainly from corn. The production process includes grinding, cooking, saccharification, fermentation, and distillation. Food-grade alcohol production requires further rectification to remove volatile organic impurities to satisfy the current 280 million gallon in the US. These impurities could be of health concern and/or impart unpleasant taste and odor in beverage alcohol. Today, these undesirable compounds are removed through multiple distillation (Sobocan and Glavic, 2000). However, this purification method increases the cost of alcohol.

On the other hand, ozone treatment is very popular for water and wastewater treatment as an effective and economical purification method. Ozone, O_3, is a triatomic molecule, consisting of three oxygen atoms. It is an allotrope of oxygen that is much less stable than the diatomic species, O_2. The gas has pale color and a unique odor. Ozone has a very high oxidation potential, second only to the hydroxyl free radical. This is derived from the oxidative activity of ozone and oxidizing spaces produced by ozone such as $OH^{\bullet}$ radicals (Sangave, et al., 2006). Therefore, ozone can oxidize many organic and inorganic compounds. Also, due to its unstable composition, it decomposes over time, so there is no residue after the treatment. For these reasons, ozone is utilized for many purposes such as disinfection, discoloration, and deodorization. A significant decrease in toxins and toxicity in water is observed with ozonation in water treatment (Brooke et al., 2006). Also, it is estimated that the cost of ozone treatment for wastewater and sludge was only 0.0437 cents/gallon against the distillation cost, which is believed to be approximately 30 cents/gallon (He et al., 2006).

It is expected that ozone can remove impurities, such as azeotropes, which cannot be removed through distillation. An azeotrope is a mixture of more than 2 compounds whose mole fractions in the vapor phase and liquid phase are same, which means those compounds cannot be separated through distillation. Azeotropes become a problem when making ethanol concentration higher through distillation. Ethanol and water consist of an azeotrope. Thus, 200 proof ethanol cannot be obtained only with distillation. However, the problem is not only with water. Ethanol makes azeotropes with other compounds, especially those whose boiling points are similar to ethanol. Table 1 is a list of examples of azeotropic compounds of ethanol. Some compounds are of health concern, such as benzene. Ozone has a possibility to remove those compounds.

Table 1: Azeotropic compounds of ethanol (ECOSSE, 2001)

Chemical Compound	Boiling Point (°C)	Azeotrope (compound + ethanol) Boiling Point (°C)		Chemical Compound	Boiling Point (°C)	Azeotrope (compound + ethanol) Boiling Point (°C)
Isoprene	34.0	32.7		Cyclohexane	81.4	64.9
Bromoethane	38.0	37.0		Acetonitrile	82.0	72.9
Dichloromethane	40.1	39.9		Vinylisobutyl-Ether	83.4	69.2
Iodomethane	42.5	41.2		1,2-Dichloroethane	83.5	70.5
Carbon Disulfide	46.3	42.4		Ethylene-Dichloride	84.0	71.0
1,1,2-Trichloro-Trifluoroethane	47.7	43.8		Thiophene	84.1	70.0
2-Bromopropane	48.4	46.2		Trichloroethylene	87.0	70.9
Chloroform	61.2	59.4		Diethyl-Formal	87.5	74.2
Vinylpropyl-Ether	65.1	60.0		2,3-Butanedione	88.0	73.9
Isopropyl-Ether	67.5	64.0		Ethyl-Nitrate	88.7	71.9
Isobutyl-Chloride	68.9	61.3		Isopropyl-Acetate	89.0	76.8
Hexane	69.0	58.7		Triethyl-Amine	89.5	76.9
Methylbutyl-Ether	70.3	65.5		Bromodichloromethane	90.2	75.5
Iodoethane	72.2	63.0		Ethylbutyl-Ether	92.2	73.8
Butryaldehyde	75.7	70.7		Vinylbutyl-Ether	94.2	73
Carbon Tetrachloride	76.8	65.0		Dibromomethane	98.2	76
Butylamine	77.1	82.2		Heptane	98.4	72
Ethyl-Acetate	77.2	71.8		Ethyl-Acrylate	99.3	77.5
Ethanol	**78.0**	78.0		Water	100	**78.2**
1-Chlorobutane	78.0	65.7		Nitromethane	101	76
Methylethyl-Ketone	79.6	74.8		1-Bromobutane	101.55	75
Benzene	80.2	67.8		Toluene	110.6	76.7
Methyl-Acrylate	80.9	73.5		Tetrachloroethylene	121	76.8

However, ozone will typically not remove impurities completely. Some compounds are very stable so that they are not oxidized by ozone. Those that are oxidized are not completely mineralized to carbon dioxide and water and ozonolysis byproducts result. Most of these would not be problematic, but it may also be possible to remove many of these by adsorption. Activated carbon provides high porosity with a wide range of pore sizes with a resultant huge surface area, between $300m^2/g$ and $2000m^2/g$ (USDA, 2006). These characteristics allow activated carbon to adsorb huge amounts of a broad range of compounds. As an example of a combination of ozone and GAC, it is found that activated carbon can provide additional adsorption and catalytic degradation of organic compounds from wastewater, utilized with ozone treatment (Lin and Wang, 2003).

While the less costly methods are well developed in water and wastewater treatment industries, these approaches have not been introduced to the bioethanol industry. The research at Iowa State University, described in this paper, is the first public release of the results of such studies.

All chemical and sensory analyses were completed by using solid-phase microextraction (SPME) to extract volatile organic compounds (VOCs) from ethanol samples followed by a multidimensional GC-MS-Olfactometry system to identify impurities and the nature of odorous compounds. SPME is a solvent-free extraction technique. It is coated by a solid, liquid, or a combination of the two. This coating can collect compounds by absorption or adsorption. Also, SPME has very sensitive trace ability down to ppb levels. It can be applied to a wide range of VOCs (from polar to non-polar materials) which can be characterized by mass spectrometry (Thiebaut et al., 2007). SPME is therefore a suitable sampling method for odor analysis since it does not require any special treatment. SPME fiber absorbs or adsorbs VOCs from the headspace without any solvent.

The purpose of this research is to investigate the ozone and activated carbon treatment to purify the fuel grade ethanol to pharmaceutical and beverage grade ethanol. This technology will help the corn milling and ethanol industry and provide an opportunity for improving the long-term sustainability of corn growing and processing.

2. Experimental

2.1 Calibration of ozone concentrations and doses with titration

Ozone production, as generated by our ozone generators (OZX-300U, Enaly, Minghang District, Shanghai, China) were confirmed using titration method before each treatment. These ozone generators are regulated with separate variable transformers and air that is used in ozone generation is first desiccated by passing through activated alumina. The ozone generators were calibrated by passing the ozonated gas through 200 mL 2% *potassium iodide* water solution (KI). Ozone reacts with I^- and the following reaction occurs:

$$O_3+2I^-+H_2O \Rightarrow I_2+O_2+2OH^-$$

With the progress of ozonation, the color of the KI solution changes into the yellow iodine color. This reaction was facilitated at room temperature using a specific time, i.e., 5, 10 and 20 minutes during which the ozone generators were monitored for consistent output. After the end of the specified time, we added 10 mL of 2M H_2SO_4 to the solution. Then, we titrated with 0.05M

$Na_2S_2O_3$ until the yellow iodine color almost disappeared. After that, we added 2mL 1% starch indicator to form a more readily seen blue complex with iodine. The solution was titrated to the disappearance of the blue color. This approach allowed us to quantify iodine amount by adding $Na_2S_2O_3$ according to the following reaction:

$$I_2 + 2S_2O_3^{2-} \Rightarrow 2I^- + S_4O_6^{2-}$$

Ozone was applied to alcohol samples (See Table 1 and Figures1 and 2 for testing procedures) and the dose was then calculated with the following equation:

$$\text{Ozone dose, mg/min} = \frac{A \times N \times 24}{T}$$

Where:

A = the amount of the titrant, $Na_2S_2O_3$, mL

N = the concentration of titrant, $Na_2S_2O_3$, mol/L

T = ozonation time, min

The factor 24 originates from the ozone molecular mass (48) divided by the number of electrons (2) transferred

2.2 Schematic of treatment

We passed ozone gas through 200 mL sample inside a 250ml tall form gas washing bottle (from Corning, Corning, NY) for a specific time depending on the ozone dosage. Additional treatment with granular activated carbon (GAC) (F-400, Calgon carbon, Pittsburgh, PA) was also used for the subset of samples.

This was accomplished by adding 40 g of GAC to 200 mL of sample inside a 250 mL Erlenmeyer flask, and the flask was agitating at 220 rpm for 10 minutes. Samples (25 mL) were collected after the ozone treatment and after the GAC treatment with a 25 ml pipette(from Fisher Scientific, Hampton, NH) and transferred to 40 mL amber glass vials equipped with PTFE coated septa (from Supelco, Bellefonte, PA). 20 mm long, polygon stir bars (from Fisher Scientific, Hampton, NH).

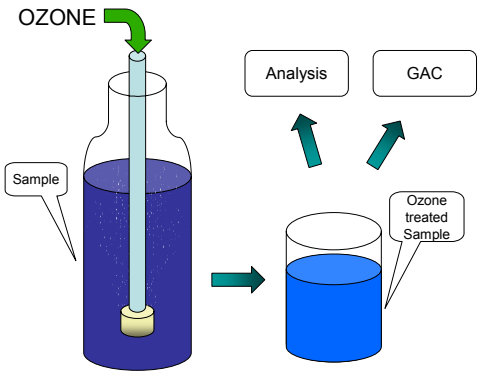

Figure 1 Schematic view of treatment: Ozonation

2.3 SPME

Solid phase microextraction (SPME) was used for all samples to extract and preconcentrate volatile organic compounds (VOCs) from samples. We used 85um Carboxen/PDMS fiber (57334-U, Supelco, Bellefonte, PA). The pore size of Carboxen/PDMS (2–20 A°) is ideal for trapping small molecules and its high porosity provides a large surface area. The pores pass through the phase particles facilitating rapid desorption . These fibers have high sensitivity for volatile acids and alcohols (< C8) (10 ppt –1 ppm), C2 –C8 aldehydes (1–500 ppb) and C3 –C9 ketones (5 ppb–1 ppm). So we selected Carboxen/PDMS fiber because of its broad specificity and sensitivity.

All samples were collected by headspace extraction with SPME. First, all samples were stirred for 10 min at 850 rpm using an advanced multi-position stirrer (VWR, West Chester, PA), SPME fiber was inserted through septum using fixed 2 cm depth and 10 min sampling time. After extraction, we immediately transferred SPME and inserted it into GC-MS-O for separation and analysis.

2.4 GC-MS-O

Multidimensional GC-MS-O (Microanalytics, Round Rock, TX) was used for all analyses. The system integrates GC-O with conventional GC-MS (Agilent 6890N GC / 5973 MS, Wilmington, DE, USA) as the base platform with the addition of an olfactory port and flame ionization detector (FID). The system was equipped with a non-polar precolumn and polar analytical column in series as well as system automation and data acquisition software (MultiTrax™ V. 6.00 and AromaTrax™ V. 6.61, Microanalytics and ChemStation™, Agilent). The general run parameters used were as follows: injector, 260 °C; FID, 280 °C, column, 40 °C initial, 3 min hold, 7 °C /min, 220 °C final, 10 min hold; carrier gas, He. Mass to charge ratio (m/z) range was set between 33 and 280. Spectra were collected at 6 scans/sec and electron multiplier voltage was set to 1500 V. The MS detector was auto-tuned weekly.

The identity of compounds was verified using (a) reference standards (Sigma-Aldrich, Fisher, Fluka) and matching their retention time on multidimensional GC capillary column and mass spectrums; (b) matching mass spectrums of unknown compounds with BenchTop/PBM (Palisade Mass Spectrometry, Ithaca, NY, USA) MS library search system and spectrums of pure compounds, and (c) by matching the description of odor character.

Human panelists were used to sniff separated compounds simultaneously with chemical analyses. Odor evaluations consisted of qualitative comparisons of (a) the number of separated odor events and (b) the total odor defined here as sum of the product of odor intensity and odor event duration for all separated odor events recorded in an aromagram. An aromagram was recorded by a panelist utilizing the human nose as a detector. Odor events resulting from separated compounds eluting from the column were characterized for odor descriptor with a 64-descriptor panel and odor intensity with Aromatrax software (Microanalytics, Round Rock, TX). The olfactory responses of a panelist were recorded using Aromatrax software by applying an odor tag to a peak or a region of the chromatographic separation. The odor tag consisted of editable odor character descriptors, an odor event time span (odor duration) and perceived odor intensity.

2.5 Data Analysis

The relative % reduction was used to evaluate the effectiveness of different ozone application rates. Treatment effectiveness of total VOCs and potential odor control measured with the GC-

O approach was expressed as percent reduction, i.e., as the ratio of the difference between the control and treatment to the control, of the form:

$$\%Reduction = \frac{C - T}{C} \times 100\% \quad [1]$$

where:

C = peak area count of total VOCs (excluding ethanol) or odor for the contaminated alcohol, and

T = peak area count of total VOCs (excluding ethanol) or odor for the ozone-treated contaminated alcohol.

2.6 Setup to provide purer feed gas to ozone generator

A purer feed gas providing setup was built to avoid contamination from the room air. Air or oxygen was provided from a gas cylinder, and from each gas, moisture and hydrocarbon were removed through a moisture trap (from Restek, State College, PA) and a hydrocarbon trap (from Restek, State College, PA). Gas flow was controlled by a mass flow controller. The quality of feed gas and ozone produced from those feed gas were evaluated by SPME-GC-MS-O.

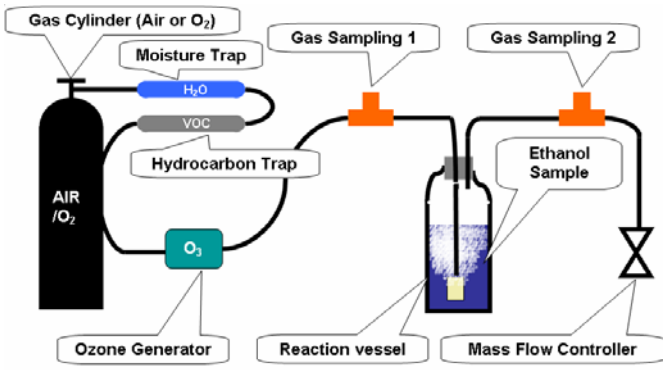

Figure 2: Setup to provide purer feed gas to ozone generator

2.7 Designing a ozone generator providing purer ozone gas

A new ozone generator was designed to generate purer ozone gas. This ozone generator was consisted of a stainless steel tubing (O.D. 12.7mm, I.D. 10.9mm), glass tubing, steel wool, and a high voltage transformer, which was taken from a ozone generator, OZX-300U.

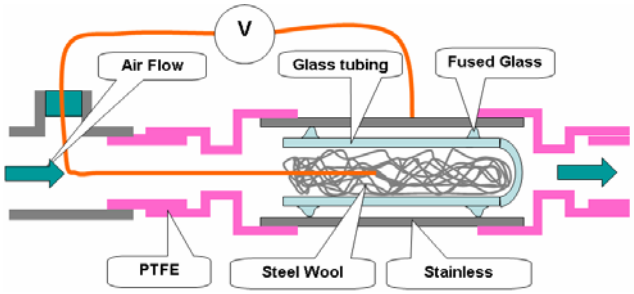

Figure 3: Ozone generator providing purer ozone gas

3. Result and Discussion

3.1 Ozone and GAC treatment

3.1.1 165 proof industrial ethanol

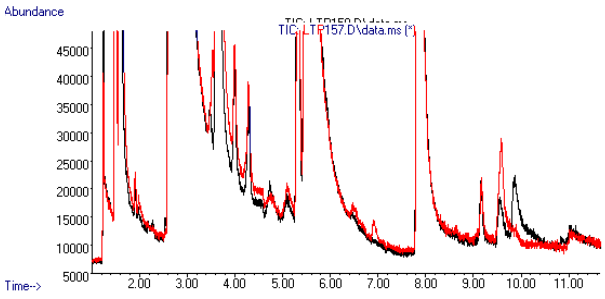

Figure 4: GC-TIC: Control without GAC (black) vs. 160 mg/L without GAC (red)

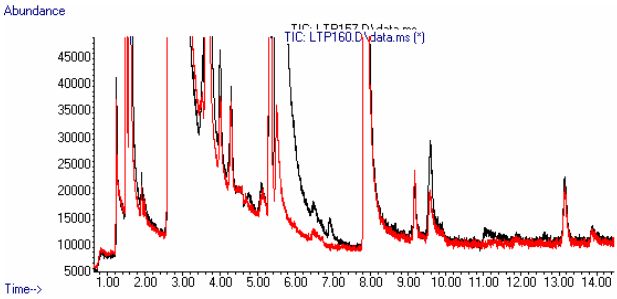

Figure 5: GC-TIC: 160 mg/L without GAC (black) vs. 160 mg/L with GAC (red)

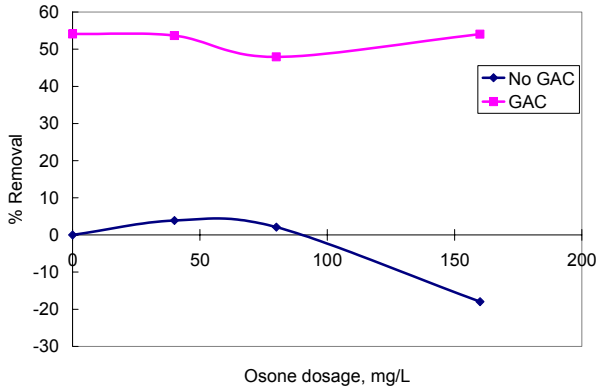

Figure 6: Total % Removal (Blue: No GAC, Red: GAC)

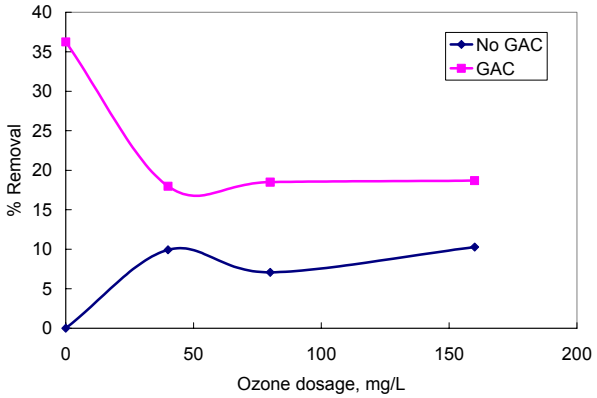

Figure 7: % Removal of Isoamyl Alcohol (Blue: No GAC, Red: GAC)

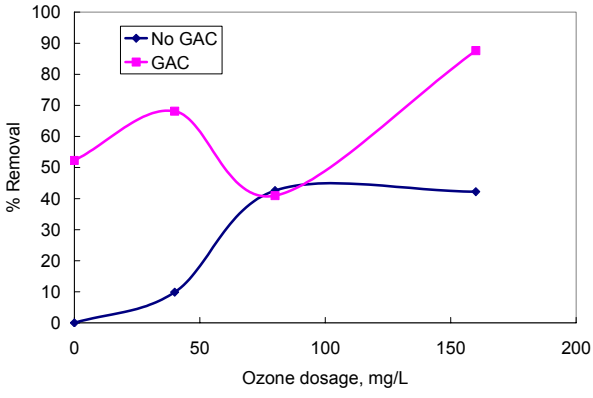

Figure 8: % Removal of 3-Methyl-Thiophone (Blue: No GAC, Red: GAC)

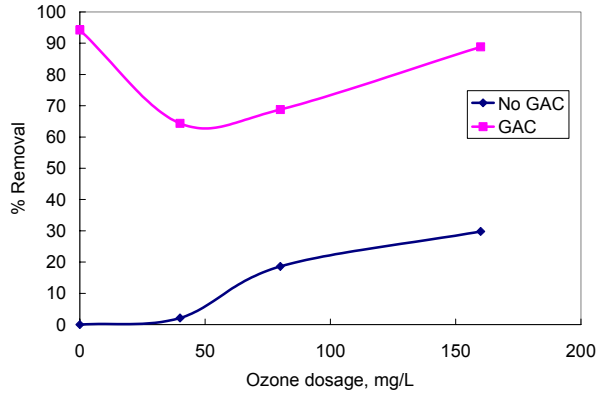

Figure 9: % Removal of Dimethyl Trisulfide (Blue: No GAC, Red: GAC)

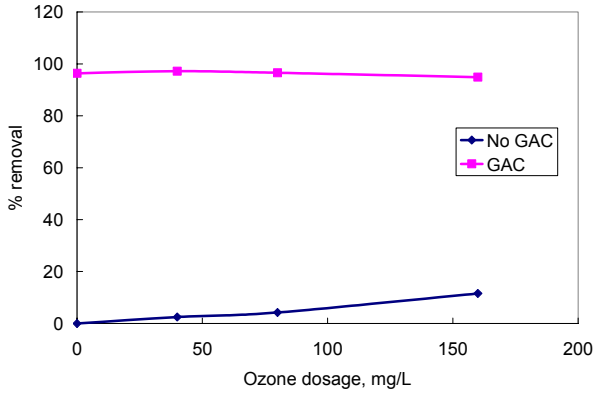

Figure 10: % Removal of Methyl-Benzene (Blue: No GAC, Red: GAC)

From the stand point of the % removal of total VOCs, it looks like ozone does not work very well (Figure 4 and 6) while GAC removes VOCs very effectively (Figure 5 and 6). However, if we focus on each VOC, ozone removes some VOCs very effectively (Figure7, 8, and 9). Also, for some compounds such as Methyl-Benzene, ozone does not work at all while GAC works very well.

These results can be considered that ozone removed some impurities from ethanol samples. However, it is also true that ozone treatment added some impurities in ethanol. Several reasons can be considered. One is that ozone produce ozonolysis byproduct by reacting with impurities. Another one is that simply the feed gas was not clean, so some compounds in atmospheric air were introduced into ethanol through babbling step. We considered the purity of ozone gas was the main reason of additional impurities. Then, we built a setup to provide purer feed gas to ozone generator.

3.2 Setup to provide purer feed gas to ozone generator

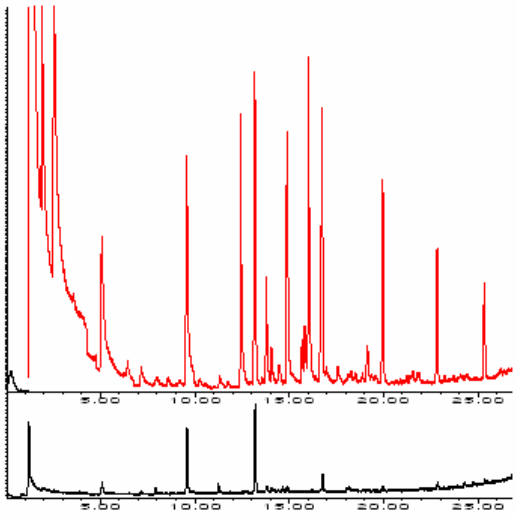

Figure 11: Air provided by purer feed gas setup (black) vs. Ozone generated from air by OZX-300U (red)

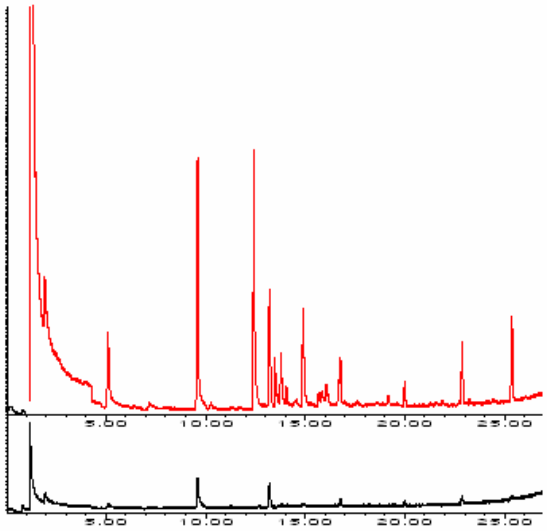

Figure 12: Oxygen provided by purer feed gas setup (black) vs. Ozone generated from oxygen by OZX-300U (red)

From figure 11 and 12, we can say the gases provided by the setup were pure enough as feed gases. However, the ozone generated from these pure feed gases includes so many impurities. It can be considered that the ozone generator, OZX-300U, introduced impurities in the gas. The ozone generating part of OZX-300U is consisted of metal, plastic, and glue. These components, especially plastic and glue, can be subject of oxidation. The impurities observed in ozone gas are ozonolysis compounds derived from these components.

3.3 Designing a ozone generator providing purer ozone gas

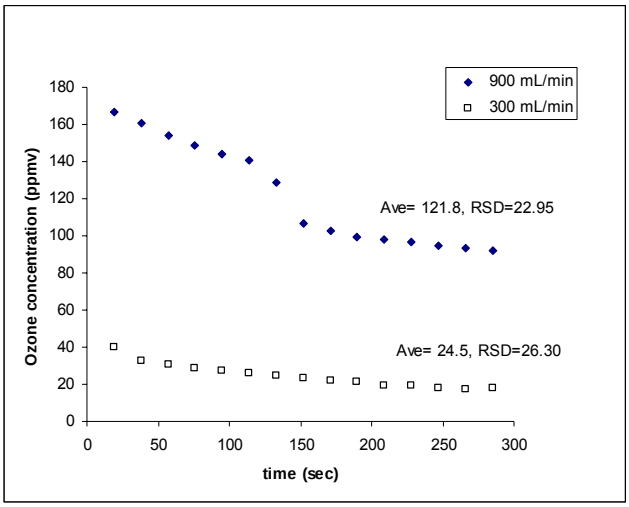

Figure 13: ozone concentration generated by original design ozone generator from air (7mm O.D. glass tubing)

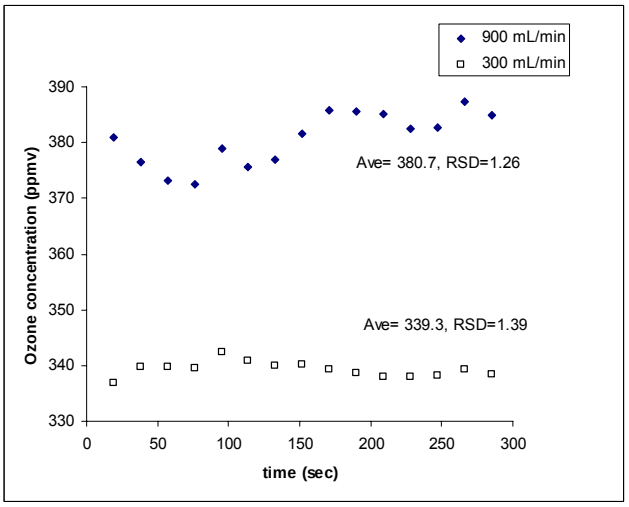

Figure 14: ozone concentration generated by original design ozone generator from air (7mm O.D. glass tubing)

So far, we achieved to generate approximately 380 ppmv of ozone by our original ozone generator (7 mm O.D. glass tubing). The concentration of ozone gas varies depending on the position of ozone generator or its running time. It is required to make the ozone output stable to use this ozone generator for research.

4. Conclusion

An ethanol purification method using ozone gas and granular activated carbon (GAC) was evaluated. With an increase of ozone dosage, the percent reduction of some impurities in ethanol samples increased. However, ozone works selectively. Some compounds could not be removed very well. While ozone has a selective characteristic, GAC works non-selectively. Most impurities are removed by GAC. Also, it was very effective remove ozonolysis byproducts.

We also found that non-pure feed gas and some components in ozone generator could result in introduction of impurities into the ethanol samples. Our purer feed gas providing setup achieved to provide highly pure feed gas to an ozone generator. Also, the new ozone generator designed by the research team could generate purer ozone gas. These new setup will provide more accurate results on this research, the purification of ethanol using ozone and GAC.

5. References

Brooke, S., G. Newcombe, B. Nicholson, G. Klass. 2006. Decrease in toxicity of microcystins LA and LR in drinking water by ozonation. *Toxicon* 48: 1054-1059.

ECOSSE. 2001. Azeotrope Databank: The Edinburgh Collection of Open Software for Simulation and Education. Available at: http://eweb.chemeng.ed.ac.uk/. Accessed 22 April 2007.

He, S., G. Xue, B. Wang. 2006. Activated sludge ozonation to reduce sludge production in membrane bioreactor (MBR). *Journal of Hazardous Materials.* B135. 406-411.

Lin, S.H., C.H. Wang. 2003. Industrial wastewater treatment in a new gas-induced ozone reactor. *Journal of Hazardous Materials.* B98: 295-309.

Sangave, P.C., P.R. Gogate, A.B. Pandit. 2006. Ultrasound and ozone assisted biological degradation of thermally pretreated and anaerobically pretreated distillery wastewater. *Chemosphere.* 68: 42-50.

Sobocan, G., P. Glavic. 2000. Optimization of ethanol fermentation process design. *Applied Thermal Engineering*. 20: 529-543.

Thiebaut, B., A. Lattuati-Derieux, M. Hocevar. 2007 Application of headspace SPME-GC-MS in characterization of odorous volatile organic compounds emitted from magnetic tape coatings based on poly(urethane-ester) after natural and artificial ageing. *Polymer Testing*. 26, 243-256

USDA. 2006. Biofuels Testimony 9-6-2006: United States Department of Agriculture. Available at: http://www.usda.gov. Accessed 7 April 2007.

USDA. 2006. Activated Carbon 6-13-2006: United States Department of Agriculture. Available at: http://www.ams.usda.gov. Accessed 9 April 2007.